Fuel Composition

The present invention relates to a fuel composition containing, 5 as major component, a specific gasoline and, as minor component, selected gasoline additives.

Carburettors and inlet systems of Otto engines, and also injection systems for fuel proportioning, are subjected to increasing load due to contamination caused by dust particles from the air, unburned hydrocarbon residues from the combustion chamber and crankcase breather gases passed to the carburettor.

These residues shift the air-to-fuel ratio during idling and in

15 the lower partial load region, so that the mixture becomes leaner
and combustion less complete and consequently the content of unburned or partly burned hydrocarbons in the exhaust gas increases
and the gasoline comsumption rises.

20 It is known to avoid these drawbacks by using fuel additives for cleaning the valves and carburettors or injection systems of Otto engines (cf eg: M. Rossenbeck in "Katalysatoren, Tenside, Mineralöladditive", edited by J. Falbe, U. Hasserodt, page 223, G. Thieme Verlag, Stuttgart 1978).

Furthermore, the problem of valve seat wear occurs in the case of Otto engines of less recent design when fuelled with unleaded gasolines. To counteract this, anti-valve-seat-wear additives based on alkali metal or alkaline earth metal compounds have been developed.

For trouble-free running, modern Otto engines require automotive fuels having a complex set of properties which can only be guaranteed when use is made of appropriate gasoline additives. Such gasolines usually consist of a complex mixture of chemical compounds and are characterized by physical parameters. The interrelationship between gasolines and appropriate additives in known fuel compositions is still unsatisfactory as regards their detergent action or their pollution-abating properties and their anti-valve-seat-wear action.

It is thus an object of the present invention to provide a more effective gasoline/additive formulation.

45 Accordingly, we have found a fuel composition which contains, as major component, a gasoline having an aromatics content of not more than 42 vol% and a sulfur content of not more than 150 ppm

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by weight, and, as minor component, at least one gasoline additive having a detergent action or an anti-valve-seat-wear action, which gasoline additive contains at least one hydrophobic hydrocarbon group having a number-average molecular weight (M_n) of from 85 to 20,000 and at least one polar group selected from

- (a) monoamino or polyamino groups containing up to 6 nitrogen atoms, of which at least one has alkaline properties,
- 10 (b) nitro groups, optionally combined with hydroxyl groups,
 - (c) hydroxyl groups combined with monoamino or polyamino groups, in which at least one nitrogen atom has alkaline properties,
 - (d) carboxylic acid groups or the alkali metal or alkaline earth metal salts thereof,
 - (e) sulfo groups or the alkali metal or alkaline earth metal salts thereof,
 - (f) polyoxy-(C₂-C₄ alkylene) groups which are terminated by hydroxyl groups, by monoamino or polyamino groups, in which at least one nitrogen atom has alkaline properties, or by carbamate groups,
 - (g) carboxylate groups,
 - (h) groups derived from succinic anhydride and containing hydroxyl and/or amino and/or amido and/or imido groups and
 - (i) groups produced by Mannich reaction of substituted phenols with aldehydes and mono- or poly-amines.
- 35 The aromatics content of the gasoline is preferably not more than 40 vol% and more preferably not more than 38 vol%. Preferred ranges for the aromatics content are from 20 to 42 vol% and particularly from 25 to 40 vol%.
- 40 The sulfur content of the gasoline is preferably not more than 100 ppm by weight and more preferably not more than 50 ppm by weight. Preferred ranges for the sulfur content are from 0.5 to 150 ppm by weight and particularly from 1 to 100 ppm by weight.

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In a preferred embodiment, the gasoline has an olefin content of not more than 21 vol%, preferably not more than 18 vol% and more preferably not more than 10 vol%. Preferred ranges for the olefin content are from 6 to 21 vol% and particularly from 7 to 18 vol%.

In another preferred embodiment, the gasoline has a benzene content of not more than 1.0 vol% and preferably not more than 0.9 vol%. Preferred ranges for the benzene content are from 0.5 to 1.0 vol% and preferably from 0.6 to 0.9 vol%.

In another preferred embodiment, the gasoline has an oxygen content of not more than 2.7 wt%, preferably from 0.1 to 2.7 wt%, more preferably from 1.0 to 2.7 wt% and most preferably from 1.2 to 2.0 wt%.

Particular preference is given to a gasoline which has an aromatics content of not more than 38 vol% and at the same time an ole-fin content of not more than 21 vol%, a sulfur content of not more than 50 ppm by weight, a benzene content of not more than 1.0 vol% and an oxygen content of from 1.0 to 2.7 wt%.

The content of alcohols and ethers in the gasoline is normally relatively low. Typical maximum contents are methanol 3 vol%, ethanol 5 vol%, isopropanol 10 vol%, tert-butanol 7 vol%, isobutanol 10 vol% and ethers containing 5 or more carbon atoms in the molecule 15 vol%.

The summer vapor pressure of the gasoline is usually not more than 70 kPa and preferably not more than 60 kPa (at 37° C).

The research octane number ("RON") of the gasoline is usually from 90 to 100. A usual range for the corresponding motor octane number ("MON") is from 80 to 90.

35 The above characteristics are determined by conventional methods (DIN EN 228).

The hydrophobic hydrocarbon group in the gasoline additives, which provides sufficient solubility in the fuel, has a number-average molecular weight (Mn) of from 85 to 20,000, preferably from 113 to 10,000 and more preferably from 300 to 5000. Typical hydrophobic hydrocarbon groups, particularly in conjunction with the polar groups (a), (c), (h) and (i), are polypropenyl, polybutenyl and polyisobutenyl radicals having molecular weights Mn of from 300 to 5000, preferably from 500 to 2500 and more preferably from 750 to 2250.

The following examples of individual gasoline additives having a detergent action or an anti-valve-seat-wear effect are mentioned by way of example.

5 Additives containing monoamino or polyamino groups (a) are preferably polyalkene monoamines or polyalkene polyamines based on polypropylene or highly reactive (ie containing predominantly terminal double bonds - mostly in the α and β positions) or conventional (ie containing predominantly centered double bonds) poly-10 butylene or polyisobutylene having a molecular weight M_n of from 300 to 5000. Such additives based on highly reactive polyisobutylene which can be prepared from the polyisobutylene containing up to 20 wt% of n-butylene units, by hydroformylation and reductive amination with ammonia, monoamines or polyamines such as dimethylaminopropylamine, ethylenediamine, diethylenetriamine, triethylenetetramine or tetrethylenepentamine, are disclosed, in particular, in EP-A 244,616. If the synthesis of the additives is based on polybutylene or polyisobutylene having predominantly centered double bonds (mostly in the β and γ positions) as starting materi-20 als, an obvious choice is the synthesis method involving chlorination and subsequent amination, or oxidation of the double bond with air or ozone to form the carbonyl or carboxyl compound, with subsequent amination under reductive (hydrogenating) conditions. This amination may be carried out using the same amines as mentioned above for the reductive amination of hydroformylated,

Further preferred additives containing monoamino groups (a) are the hydrogenation products of the reaction products of polyisobutylenes having an average degree of polymerization P of from 5 to 100 with nitrogen oxides or mixtures of nitrogen oxides and oxygen, as described, in particular, in WO-A 97/03946.

polypropylene are described, in particular, in WO-A 94/24231.

highly reactive polyisobutylene. Corresponding additives based on

- 35 Further preferred additives containing monoamino groups (a) are the compounds produced from polyisobutylene epoxides by reaction with amines followed by dehydration and reduction of the amino alcohols, as described, in particular, in DE-A 196 20 262.
- 40 Additives containing nitro groups, optionally combined with hydroxyl groups (b), are preferably reaction products of polyisobutylenes having an average degree of polymerization P of from 5 to 100 or from 10 to 100 with nitrogen oxides or mixtures of nitrogen oxides and oxygen, as described, in particular, in WO-A
- 45 96/03367 and WO-A 96/03479. These reaction products are usually mixtures of pure nitropolyisobutanes (eg α , β -dinitropolyisobu-

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tane) and mixed hydroxynitropolyisobutanes (eg α -nitro- β -hydroxy-polyisobutane).

Additives containing hydroxyl groups combined with monoamino or polyamino groups (c) are in particular reaction products of polyisobutylene epoxides, obtainable from polyisobutylene preferably containing predominantly terminal double bonds and having a molecular weight M_n of from 300 to 5000, with ammonia or mono- or poly-amines, as described, in particular, in EP-A 476,485.

Additives containing carboxylic acid groups or the alkali metal or alkaline earth metal salts thereof (d) are preferably copolymers of C₂-C₄₀ olefins with maleic anhydride having a total molecular weight of from 500 to 20,000 whose carboxylic acid groups have been converted entirely or partially to the alkali metal or alkaline earth metal salts and the remainder of the carboxylic acid groups has been caused to react with alcohols or amines. Such additives are disclosed, in particular, in EP-A 307,815. Said additives mainly serve to prevent valve seat wear and can be used, as described in WO-A 87/01126, with advantage combined with conventional fuel detergents such as poly(iso)butylene amines or polyether amines.

Additives containing sulfo groups or the alkali metal or alkaline earth metal salts thereof (e) are preferably alkali metal or alkaline earth metal salts of an alkyl sulfosuccinate, as described, in particular, in EP-A 639,632. Such additives mainly serve to prevent valve seat wear and can be used with advantage combined with conventional fuel detergents such as poly(iso)butylene amines or polyether amines.

Additives containing polyoxy-(C_2 - C_4 alkylene) groups (f) are preferably polyethers or polyether amines, which are obtained by reaction of C_2 - C_{60} alkanols, C_6 - C_{30} alkanediols, mono- or di-(C_2 - C_{30} alkyl)amines, (C_1 - C_{30} alkyl)cyclohexanols or (C_1 - C_{30} alkyl)phenols with from 1 to 30 mol of ethylene oxide and/or propylene oxide and/or butylene oxide per hydroxyl group or amino group and, in the case of polyether amines, by subsequent reductive amination with ammonia, monoamines or polyamines. Such products are described, in particular, in EP-A 310,875, EP-A 356,725, EP-A 700,985 and US-A 4,877,416. In the case of polyethers such products also have flotation oil characteristics. Typical examples thereof are tridecanol butoxylates or isotridecanol butoxylates, isononylphenol butoxylates, polyisobutenol butoxylates and polyisobutenol propoxylates and the corresponding reaction products with ammonia.

Additives containing carboxylate groups (g) are preferably esters of mono-, di- or tri-carboxylic acids with long-chain alkanols or polyols, in particular those having a minimum viscosity of 2 mm²/s at 100°C, as described, in particular, in DE-A 3,838,918. The mono-, di- or tri-carboxylic acids used can be aliphatic or aromatic acids, and suitable ester alcohols or ester polyols are primarily long-chain representatives containing, for example, from 6 to 24 carbon atoms. Typical representatives of these esters are adipates, phthalates, isophthalates, terephthalates and trimellitates of isooctanol, isononanol, isodecanol and isotridecanol. Such products also have flotation oil characteristics.

Additives containing groups derived from succinic anhydride and containing hydroxyl and/or amino and/or amido and/or imido groups (h) are preferably corresponding derivatives of polyisobutenyl succinic anhydride, which are obtained by reaction of conventional or highly reactive polyisobutylene having a molecular weight Mn of from 300 to 5000 with maleic anhydride by thermal treatment or via chlorinated polyisobutylene. Of special interest in this respect are derivatives with aliphatic polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine or tetrethylenepentamine. Such gasoline additives are described, in particular, in US-A 4,849,572.

25 Additives containing groups (i) produced by Mannich reaction of substituted phenols with aldehydes and mono- or poly-amines are preferably reaction products of polyisobutylene-substituted phenols with formaldehyde and mono- or poly-amines such as ethylene-diamine, diethylenetriamine, triethylenetetramine, tetrethylene-pentamine or dimethylaminopropylamine. The polyisobutenyl-substituted phenols can be derived from conventional or highly reactive polyisobutylene having a molecular weight Mn of from 300 to 5000. Such "polyisobutylene Mannich bases" are described, in particular, in EP-A 831,141.

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To provide a more precise definition of the individual gasoline additives mentioned above, the disclosures of the aforementioned specifications of the prior art are included herein by reference.

40 The fuel composition of the invention can contain yet other conventional components and additives. Foremost examples thereof are flotation oils not having any marked detergent action, for example mineral flotation oils (base oils), in particular those of the viscosity class "Solvent Neutral (SN) 500 to 2000", and synthetic flotation oils based on olefin polymers having a molecular weight Mn of from 400 to 1800, mainly based on polybutylene or

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polyisobutylene (hydrogenated or non- hydrogenated), on $poly(\alpha-olefin)s$ or poly(internal olefin)s.

Suitable solvents or diluents (for use in additive packs) are aliphatic and aromatic hydrocarbons, eg solvent naphtha.

Further conventional additives are corrosion inhibitors based, for example, on film-forming ammonium salts of organic carboxylic acids or heterocyclic aromatics for nonferrous metal corrosion protection, antioxidants or stabilizing agents based, for example, on amines such as p-phenylenediamine, dicyclohexylamine or derivatives thereof or phenols such as 2,4-di-tert-butylphenol or 3,5-di-tert-butyl-4-hydroxyphenylpropionic acid, demulsifiers, antistatic agents, metallocenes such as ferrocene or methylcyclopentadienyl manganese tricarbonyl, lubricity additives such as specific fatty acids, alkenyl succinates, bis(hydroxyalkyl)fatty amines, hydroxyacetamide or castor oil and also colorants (labels). Sometimes amines are also added to lower the pH of the automotive fuel.

Other suitable fuel compositions of the invention comprise, in particular, blends of the gasoline described above with a mixture of gasoline additives containing the polar group (f) and corrosion inhibitors and/or lubricity improvers based on carboxylic acids or fatty acids, which can be present as monomeric and/or dimeric species. Typical mixtures of this type contain polyisobutylene amines combined with alkanol-initiated polyethers such as tridecanol or isotridecanol butoxylates or propoxylates, polyisobutylene amines combined with alkanol-initiated polyether amines 30 such as reaction products of tridecanol or isotridecanol butoxylate with ammonia and alkanol-initiated polyether amines such as reaction products of tridecanol or isotridecaol butoxylate with ammonia combined with alkanol-initiated polyethers such as tridecanol or isotridecanol butoxylates or propoxylates, in each case combined with said corrosion inhibitors or lubricity improvers. 35

Said gasoline additives containing the polar groups (a) to (i) and said other components are metered to the gasoline, where they become effective. The components or additives can be added to the gasoline individually or as a previously prepared concentrate (additive pack).

Said gasoline additives containing the polar groups (a) to (i) are added to the gasoline usually in an amount of from 1 to 5000 ppm by weight, preferably from 5 to 3000 ppm by weight and more preferably from 10 to 1000 ppm by weight. The other compo-

nents and additives mentioned, if desired, are added in conventional amounts.

The fuel composition of the invention surprisingly allows for the use of distinctly less detergent or anti-valve-seat-wear agent to achieve the same detergent or pullution-abating action or anti-valve-seat-wear action as in the case of conventional fuel compositions of the prior art. Furthermore when the same amounts of detergent or anti-valve-seat-wear agent are used in the fuel composition of the invention as in conventional fuel compositions there is achieved, surprisingly, a distinctly better detergent or pollution-abating or anti-valve-seat-wear action.

Furthermore, the fuel composition of the invention has additional advantages in that less sedimentation occurs in the combustion chamber of the Otto engine and less additive migrates to the motor oil due to fuel dilution.

The invention is illustrated by, but not restricted to, the fol-20 lowing examples.

Examples:

The gasolines used were those listed in Table 1 complying to the specifications stated, where OF 1 stands for a typical commercial Otto fuel.

Table 1

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J	v	

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Grading	OF1 (for comparison)	OF2 (invention,)	
aromatics content [vol%]	48.4	41.8	
penzene content [vol%]	2.0	1.0	
olefin content [vol%]	22.6	7.8	
oxygen content [wt%]	0.5	1.7	
sulfur content [ppm by weight]	245	90	
summer vapor pressure (at 37°C) [kPa]	78.4	69.3	

Preparation of the fuel compositions

Example 1 (comparative example)

5 700 mg of a polyisobutylene amine, prepared from highly reactive polyisobutylene having a molecular weight M_n of 1000 by hydroformylation and subsequent reductive amination with ammonia and dilution to equal parts by weight with $C_{10}-C_{14}$ paraffin (Kerocom® PIBA sold by BASF Aktiengesellschaft), were dissolved in 1 kg of 10 OF1 as indicated in Table 1.

Example 2 (invention)

700 mg of the same polyisobutylene amine as used in Example 1 15 were dissolved in 1 kg of OF2 as indicated in Table 1.

Example 3 (comparative example)

600 mg of a commercial additive formulation for gasolines, con20 taining a conventional amount of a detergent containing carbamate
groups as in group (f), were dissolved in 1 kg of OF1 as indicated in Table 1.

Example 4 (invention)

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600 mg of the same commercial additive formulation for gasolines as used in Example 3 were dissolved in 1 kg of OF2 as indicated in Table 1.

30 Example 5 (comparative example)

400 mg of a commercial additive formulation for gasolines, containing a detergent, prepared by chlorination and subsequent amination of polyisobutylene having a molecular weight $M_{\rm n}$ of 950 and having predominantly centered double bonds, were dissolved in 1 kg of OF1 as indicated in Table 1.

Example 6 (invention)

40 400 mg of the same commercial additive formulation for gasolines as used in Example 5 were dissolved in 1 kg of OF2 as indicated in Table 1.

Example 7 (comparative example)

750 mg of a commercial additive formulation for gasolines, containing 50 wt% of the same polyisobutylene amine as used in Example 1 and also mineral and synthetic flotation oils and corrosion control agents (Keropur® 3222 sold by BASF Aktiengesellschaft) in conventional amounts, were dissolved in 1 kg of OF1 as indicated in Table 1.

10 Example 8 (invention)

350 mg of the same commercial additive formulation for gasolines as used in Example 7 were dissolved in 1 kg of OF2 as indicated in Table 1.

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Example 9 (comparative example)

500 mg of a commercial additive formulation for gasolines, containing 60 wt% of the same polyisobutylene amine as used in Example 1 and also mineral flotation oil and corrosion control means (Keropur® 3233 sold by BASF Aktiengesellschaft) in conventional amounts, were dissolved in 1 kg of OF1 as indicated in Table 1.

Example 10 (invention)

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500 mg of the same commercial additive formulation for gasolines as used in Example 9 were dissolved in 1 kg of OF2 as indicated in Table 1.

30 Example 11 (comparative example)

700 mg of a mixture of 50 wt% of the same polyisobutylene amine as used in Example 1 and 50 wt% of a commercial antiwear additive (Kerocom® 3280 sold by BASF Aktiengesellschaft) were dissolved in 1 kg of OF1 as indicated in Table 1.

Example 12 (invention)

700 mg of the same additive formulation for gasolines as used in 40 Example 11 were dissolved in 1 kg of OF2 as indicated in Table 1.

Working tests

Example 13 (comparative example)

5 Gasoline of Example 1 was examined as regards its suitability for maintaining a clean inlet system. This was done by carrying out engine tests in the form of bench tests employing a Mercedes-Benz engine CEC F-05-A-93. As expected, the deposits on the inlet valves were distinctly less than the basic value obtained when no additive is used, as shown in Table 2 below.

Example 14 (invention)

Gasoline of Example 2 was examined as regards its suitability for maintaining a clean inlet system. This was done by carrying out engine tests in the form of bench tests on a Mercedes-Benz engine CEC F-05-A-93. As expected, the deposits on the inlet valves were distinctly less than the basic value obtained when no additive is used, as shown in Table 2 below. It was surprising to find that compared with Example 13 perfect cleaning of the inlet valves is achieved using the same amount of fuel additive.

Example 15 (comparative example)

25 Gasoline of Example 3 was examined to determine its suitability for maintaining a clean inlet system. This was done by carrying out engine tests in the form of bench tests on a Mercedes-Benz engine CEC F-05-A-93. As expected, the deposits on the inlet valves were distinctly less than the basic value obtained when no additive is used, as shown in Table 2 below.

Example 16 (invention)

Gasoline of Example 4 was examined to determine its suitability

for maintaining a clean inlet system. This was done by carrying out engine tests in the form of bench tests on a Mercedes-Benz engine CEC F-05-A-93. As expected, the deposits on the inlet valves were distinctly less than the basic value obtained when no additive is used, as shown in Table 2 below. It was surprising to find that compared with Example 15 virtually perfect cleaning of the inlet valves is achieved using the same amount of fuel additive.

Example 17 (comparative example)

Gasoline of Example 5 was examined to determine its suitability for maintaining a clean inlet system. This was done by carrying out engine tests in the form of bench tests on a Mercedes-Benz engine CEC F-05-A-93. As expected, the deposits on the inlet valves were distinctly less than the basic value obtained when no additive is used, as shown in Table 2 below.

10 Example 18 (invention)

Gasoline of Example 6 was examined to determine its suitability for maintaining a clean inlet system. This was done by carrying out engine tests in the form of bench tests on a Mercedes-Benz engine CEC F-05-A-93. As expected, the deposits on the inlet valves were distinctly less than the basic value obtained when no additive is used, as shown in Table 2 below. It was surprising to find that compared with Example 17 virtually perfect cleaning of the inlet valves is achieved using the same amount of fuel additive.

Example 19 (comparative example)

Gasoline of Example 7 was examined to determine its suitability for maintaining a clean inlet system. This was done by carrying out engine tests in the form of bench tests on a Mercedes-Benz engine CEC F-05-A-93. As expected, the deposits on the inlet valves were distinctly less than the basic value obtained when no additive is used, as shown in Table 2 below.

Example 20 (invention)

Gasoline of Example 8 was examined to determine its suitability for maintaining a clean inlet system. This was done by carrying out engine tests in the form of bench tests on a Mercedes-Benz engine CEC F-05-A-93. As expected, the deposits on the inlet valves were distinctly less than the basic value obtained when no additive is used, as shown in Table 2 below. It was surprising to find that distinctly less fuel additive is required than in Example 19 to achieve a similar degree of inlet valve cleanliness.

Example 21 (comparative example)

Gasoline of Example 9 was examined to determine its suitability for maintaining a clean inlet system. This was done by carrying out engine tests in the form of bench tests on a Mercedes-Benz engine CEC F-05-A-93. As expected, the deposits on the inlet

valves were distinctly less than the basic value obtained when no additive is used, as shown in Table 2 below.

Example 22 (invention)

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Gasoline of Example 10 was examined to determine its suitability for maintaining a clean inlet system. This was done by carrying out engine tests in the form of bench tests on a Mercedes-Benz engine CEC F-05-A-93. As expected, the deposits on the inlet 10 valves were distinctly less than the basic value obtained when no additive is used, as shown in Table 2 below. It was surprising to find that compared with Example 21 distinctly better cleaning of the inlet valves is achieved using the same amount of fuel additive.

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Example 23 (comparative example)

Gasoline of Example 11 was examined to determine its suitability for maintaining a clean inlet system. This was done by carrying 20 out engine tests in the form of bench tests on a Mercedes-Benz engine CEC F-05-A-93. As expected, the deposits on the inlet valves were distinctly less than the basic value obtained when no additive is used, as shown in Table 2 below.

25 Example 24 (invention)

Gasoline of Example 12 was examined to determine its suitability for maintaining a clean inlet system. This was done by carrying out engine tests in the form of bench tests on a Mercedes-Benz 30 engine CEC F-05-A-93. As expected, the deposits on the inlet valves were distinctly less than the basic value obtained when no additive is used, as shown in Table 2 below. It was surprising to find that compared with Example 23 distinctly better cleaning of the inlet valves was achieved using the same amount of fuel addi-

35 tive.

Table 2

Additive	Dosage [mg/kg]	Deposits on the inlet valves [mg/valve]				
		valve 1	valve 2	valve 3	valve 4	average
Ex. 13	700	40	157	7	87	73 (547)
Ex. 14	700	0	0	0	0	0 (239)
Ex. 15	600	19	60	86	34	50 (274)
Ex. 16	600	0	1	0	2	1 (239)
Ex. 17	400	0	75	17	182	69 (402)
Ex. 18	400	0	2	2	0	1 (239)
Ex. 19	750	31	120	111	30	73 (592)
Ex. 20	350	46	68	38	67	55 (239)
Ex. 21	500	181	95	26	68	93 (475)
Ex. 22	500	27	33	14	77	38 (239)
Ex. 23	700	123	12	98	55	72 (558)
Ex. 24	700	82	12	23	22	35 (239)

(the values in brackets refer to the basic value of the automotive fuel not containing any additive)